

Technical Note: On Estimating Conditions for Simulating Velocity-Sensitive Corrosion in the Rotating Cylinder Electrode

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ABSTRACT

Simulation of velocity-sensitive corrosion in the laboratory for predicting similar corrosion in the field is of ongoing interest. Such an approach seems to be especially practical when corrosion is controlled by the rate of mass transport to or from the surface. Such control, when measured under appropriate conditions in the laboratory, should be observed in the field. The present research goal was to review equations that allow the corrosion practitioner to estimate easily velocities in the laboratory that would simulate flow conditions in other geometries.

KEY WORDS: rotating cylinder electrode, mass-transfer coefficient, pipe flow, velocity-sensitive corrosion

INTRODUCTION

Over the last 20 years, papers have appeared periodically proposing such equations. The rotating cylinder electrode has been the subject of much interest to simulate other field geometries for several reasons: it is a fairly simple apparatus to construct and use; it functions in the turbulent flow regime to very low Reynolds numbers (very low rotation rates);¹ it has uniform current distribution for electrochemical measurements;² and it obeys an easily expressed relationship between mass-transfer coefficient, Reynolds number, and Schmidt number especially for smooth cylinders. Reviews by Gabe, et al.,^{1,3-4} are excellent starting points for learning about this technology, the equations that govern its operation, and its applications.

Development of equations to relate the velocity in the field to that in the rotating cylinder electrode has involved different approaches. Those differences have led to markedly different equations and markedly different predictions of velocity. Mass-transfer-controlled corrosion usually has been the assumed mechanism. The purposes of this technical note were to compare these predictions and provide some insight into which equations might be best.

DISCUSSION

The equation derived from the study of Eisenberg, et al., for calculating the Sherwood number as a function of Reynolds and Schmidt numbers for the rotating cylinder electrode tends to be used in most of the developments.² It is valid for Reynolds numbers between $\sim 10^3$ and 10^5 . Since most of the equations are developed for estimating equivalent velocities between pipe flow and rotating cylinder electrode flow, only those two geometries were considered here. Pipe flow was assumed to be developed fully and the surfaces of both geometries were assumed to be smooth with a roughness less than the hydrodynamic boundary layer. Differences in the final relationships tended to be tied to differences in the relationships used for pipe flow. The objective was to determine which of these equations might be most appropriate.

Wranglen, et al., assumed that the Nusselt numbers (Sherwood numbers) in the pipe and rotating cylinder electrode could be set equal to each other.⁵ These authors assumed the common Chilton-Colburn relationship between the Nusselt (Sherwood) number and Reynolds and Schmidt numbers (an 0.8 expo-

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TABLE 1
Rotating Cylinder Electrode Velocity to Maintain Identical Mass Transfer Coefficients

Source	Equation
Wranglen, Berendson, and Karlberg	$u_{cyl} = (0.1571) \frac{d_{pipe}^{1.2}}{d_{cyl}} (\nu)^{-0.2} u_{pipe}^{1.2}$
Modified Wranglen, Berendson, and Karlberg	$u_{cyl} = (0.1716) \frac{d_{pipe}^{1.1429}}{d_{cyl}} (\nu)^{-0.1758} D^{0.0329} u_{pipe}^{1.1429}$
Holser, Prentice, Pond, and Guanti	$u_{cyl} = (0.1716) \frac{d_{cyl}^{0.4286}}{d_{pipe}^{0.2857}} (\nu)^{-0.1758} D^{0.0329} u_{pipe}^{1.1429}$
Chen, Moccari, and Macdonald	$u_{cyl} = (0.0492) \frac{d_{cyl}^{0.4286}}{d_{pipe}^{0.1243}} (\nu)^{-0.3186} D^{0.0143} u_{pipe}^{1.3043}$
Nesic, Solvi, and Skjerve	$u_{cyl} = (0.1066) \frac{d_{cyl}^{0.4286}}{d_{pipe}^{0.2000}} (\nu)^{-0.2657} D^{0.0371} u_{pipe}^{1.2286}$
Silverman	$u_{cyl} = (0.1185) \frac{d_{cyl}^{0.4286}}{d_{pipe}^{0.1786}} (\nu)^{-0.3357} D^{0.0857} u_{pipe}^{1.25}$

Where d is diameter (cm); D is diffusivity (cm²/s); u is velocity (cm/s); and ν is kinematic viscosity (cm²/s). The subscripts cyl and pipe represent the rotating cylinder electrode and pipe, respectively.

ment on the Reynolds number and 0.33 exponent on Schmidt number).⁶ They also assumed an 0.67 power on the Reynolds number and an 0.33 power on Schmidt numbers for the rotating cylinder electrode instead of the more commonly accepted values of 0.7 and 0.356, as derived in the Eisenberg study.

Holser, et al., assumed that for the rate of mass-transfer-controlled corrosion to be the same in the two geometries, the limiting currents as determined from, for example, polarization scans in seawater, had to be the same in the two geometries.⁷ In systems controlled by the rate of mass transfer, the limiting current is equal to the rate of mass transfer. Their proposal actually assumes similarity when the mass-transfer coefficients are the same in the two geometries since the bulk or surface concentration of the rate-controlling species (depending on whether control is cathodic or anodic) would be expected to be equal in both environments. For smooth surfaces, they suggested using the Chilton-Colburn relationship for the pipe and the Eisenberg relationship for the rotating cylinder electrode.

Chen, et al., simultaneously examined the rate of corrosion of a copper-nickel alloy in 1 M sodium chloride (NaCl) solution in a pipe, annulus, and a rotating cylinder electrode.⁸ Corrosion was controlled by the rate of mass transfer of oxygen to the surface through a surface film and the hydrodynamic bound-

ary layer. The surface film became unimportant with a Reynolds number of 10⁴. Their proposal is that equating the mass-transfer coefficients in the two geometries ensures similarity in corrosion rates. Their equation incorporated the Harriott-Hamilton correlation for the pipe that places an exponent of 0.913 on the Reynolds number and 0.346 on the Schmidt number.⁹ They again used the Eisenberg, et al., relationship for the rotating cylinder electrode and obtained good agreement among the three geometries.

Nesic, et al., examined corrosion of steel in slightly acidified NaCl with and without carbon dioxide (CO₂) in a pipe and rotating cylinder electrode.¹⁰ They indicate that for mass-transfer-controlled corrosion, equivalent velocities for the pipe and cylinder can be calculated by assuming equality of mass-transfer coefficients in both systems. They used the equation of Berger and Hau for the pipe and that of Eisenberg for the rotating cylinder.¹¹ In the Berger and Hau equation, the exponent on the Reynolds number is 0.86 at the high Schmidt numbers for liquids, and the exponent on the Schmidt number is 0.33.

Silverman examined the relationship among mass-transfer coefficient, fluid velocity, and shear stress in pipes, annuli, rotating cylinder electrodes, and the wall jet region of impinging flow.¹² He derived the relationships between the velocity in the rotating cylinder electrode and each of the other three geom-

etries by using the friction velocity and not the bulk velocity as the scaling velocity. His reasoning was that the mass-transfer boundary layer for the high Schmidt numbers found in most corroding systems lies well within the hydrodynamic boundary layer. The velocity driving mass transfer would not be the bulk velocity, but a velocity within the hydrodynamic boundary layer that should be less than the bulk velocity. The data generated in several geometries collapsed onto one line in a Sherwood number vs velocity plot when they were reduced to equivalent velocities based on equality of mass-transfer coefficients and using the derived equations.

The five equations that have been proposed to relate the velocity in a rotating cylinder electrode to the velocity in a pipe to ensure similarity in mass-transfer coefficients are listed in Table 1. They have been transformed so that velocity in the rotating cylinder electrode is a function of the velocity in the pipe. Included is a modification of the Wranglen, et al., equation derived assuming the more widely accepted Eisenberg exponents on Reynolds and Schmidt numbers. Figure 1 shows a comparison of the equivalent velocities using the equations. For this example, the following values were used: 1.9 cm for the diameter of the rotating cylinder electrode, 10 cm for the diameter of the pipe, 0.01 cm²/s for the kinematic viscosity of the liquid (approximately that of water), and 10⁻⁵ cm²/s for the diffusion coefficient of the rate-determining species (order of magnitude of that for dissolved oxygen). Figure 2 shows the same plot but with the Wranglen, et al., and modified Wranglen, et al., equations eliminated. The reason is that these two equations are derived assuming equality of Sherwood numbers and not mass-transfer coefficients. To have equal Sherwood numbers in the same environment in two different geometries, the mass-transfer coefficient becomes inversely proportional to the characteristic length dimension, in this case, diameter. Equality of Sherwood number implies that the mass-transfer coefficients are equal only when the scaling diameters are equal. Figures 1 and 2 correspond to Reynolds numbers of 10,000 to 100,000 for the pipe and ~ 1,700 to 30,000 for the cylinder, both well within the turbulent flow regime in both systems.

Differences among the equations, while being small at low Reynolds numbers, increase significantly with increasing Reynolds numbers. Choice of model significantly impacts the choice of modeling velocity or range of velocities to be used in the rotating cylinder electrode. The question is which of these equations is best. Since all of the correlations utilize the Eisenberg, et al., relationships for friction factor and mass-transfer coefficient, those expressions are not affecting the differences. They are assumed to represent the momentum and mass transfer for a smooth cylinder. The best equation(s) may be deter-

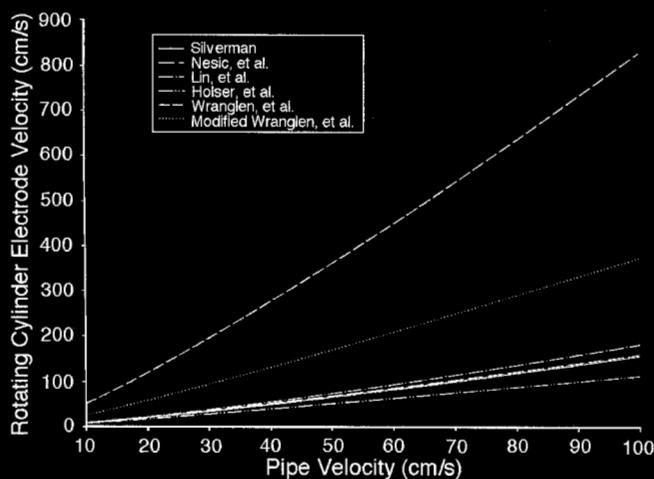


FIGURE 1. Rotating cylinder electrode velocity vs pipe velocity as predicted by equations in Table 1.

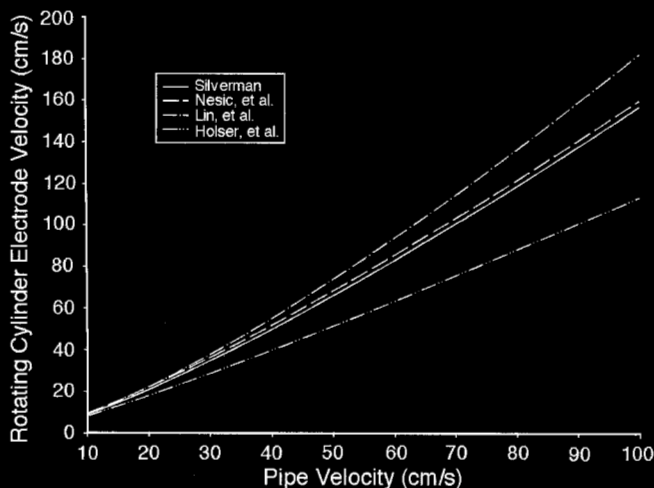


FIGURE 2. Rotating cylinder electrode velocity vs pipe velocity as predicted by equations in Table 1 with Wranglen, et al., equations eliminated.

mined by the best expression relating Sherwood and Reynolds numbers in pipe flow.

Holser, et al., use the equation derived from the Chilton-Colburn analogy among heat, mass, and momentum transfer for pipe flow. A reasonably good approximation, the equation has been reported to be in error, especially at high Schmidt numbers. The result is a tendency to underestimate the exponent on the Reynolds number in the Sherwood/Reynolds/Schmidt number relationship.^{11,13} Use of this equation would inherently produce inaccuracies in the mass-transfer coefficients of liquids, which tend to have high Schmidt numbers of the order of magnitude of 10³ to 10⁴ (e.g., aqueous type systems).

Chen, et al., used the Harriott-Hamilton equation for pipe flow and assumed that it represented the situation for smooth surfaces. That equation may not describe mass transfer in smooth pipes. Harriott and

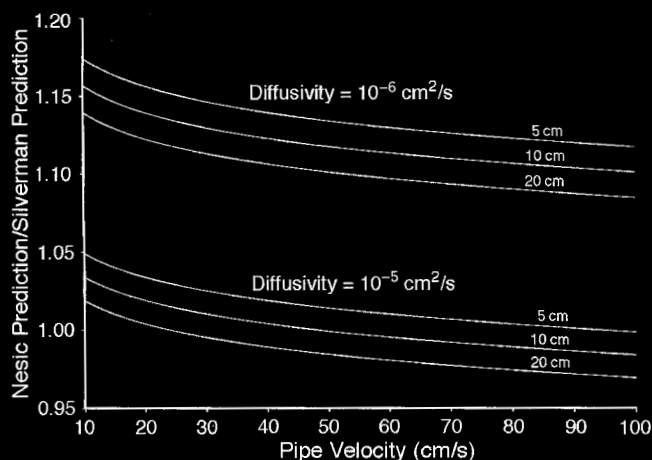


FIGURE 3. Ratio of rotating cylinder electrode velocities as predicted by the equation of Silverman divided by the equation of Nesc.

Hamilton state that the inherent roughness of the benzoic acid spool pieces they used may have influenced their results. Surface roughness would tend to increase mass-transfer rates and would be reflected in an overestimate of the exponent on the Reynolds number. The walls in this study also were somewhat porous. Porosity would affect mass-transfer rates. Errors created by these experimental artifacts were estimated to be from 0% to 10% for Schmidt numbers of 1,000, and higher for higher Schmidt numbers.⁹

Nesc, et al., used the Berger and Hau equation, which was developed using the mass-transfer-controlled ferricyanide-ferrocyanide reaction on a specially prepared surface with a roughness of $\sim 1 \mu\text{m}$. This roughness was less than the calculated boundary layer. The measurement was made in the fully developed turbulent flow portion of the pipe for a range of Schmidt numbers $> 1,000$. The exponent on the Reynolds number is a function of the Schmidt number, approaching 0.86 at high Schmidt numbers (e.g., $> \sim 10$). At low Schmidt numbers, the exponent approaches the 0.8 value of the Chilton-Colburn analogy. This equation seems to represent the Sherwood-Reynolds-Schmidt number relationship in smooth pipes for liquid systems of interest to corrosion practitioners for Reynolds numbers between $\sim 10^4$ and 10^6 .

Silverman utilized findings of Shaw and Hanratty for the mass-transfer coefficient in smooth pipes. They showed that the mass-transfer coefficient is proportional to the friction velocity for large Schmidt numbers comparable to and higher than those found in systems of interest to the corrosion practitioner.¹⁴ Their equation was verified for Reynolds numbers up to $\sim 10^5$. This implies that the mass-transfer coefficient in smooth pipes is proportional to the square root of the shear stress at the wall for high Schmidt numbers. Measurements were made using the ferricyanide/ferrocyanide reaction under fully developed

turbulent flow on a pipe wall that was polished smooth and coated with platinum. Silverman also used the relationship between the mass-transfer coefficient and the friction velocity (wall shear stress) as developed by Eisenberg, et al., for the rotating cylinder electrode. Equating the two mass-transfer coefficients led to the equation shown in Table 1.

Figure 2 shows that the Silverman and Nesc equations are in agreement. Figure 3 shows the ratio of predictions from the two equations for cases of pipe diameters of 5, 10, and 20 cm and diffusivities of $10^{-5} \text{ cm}^2/\text{s}$ and $10^{-6} \text{ cm}^2/\text{s}$. The diameter of the rotating cylinder electrode does not affect the estimate. The maximum difference is $\sim 15\%$. In view of the approximations involved in assuming that one geometry can be used to model another, at this point no statement can be made that either equation is better. Either could be used to estimate equivalent velocities to model pipe flow by the rotating cylinder electrode for the case of mass-transfer-controlled corrosion with smooth walls to pipe Reynolds numbers of at least 10^5 . The fact that corroding walls sometimes are roughened adds complexity to this approach. If such roughness is observed in practice, these equations may provide only the order of magnitude of the appropriate velocity to use in the laboratory. The best practical approach might be to examine several velocities that span the desired velocity over about an order of magnitude.

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